

## A New Cathode Material $(\text{La,Sr})_{1-z}(\text{Mn}_{1-y}\text{Cr}_y)\text{O}_3$ ( $0 \leq y \leq 0.2$ ) for SOFC

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The properties of La-Sr-Mn-Cr-O system have been investigated to search for a new air electrode material of Solid Oxide Fuel Cells (SOFC) having chemical and morphological stabilities. Measured sintering behavior of  $\text{La}(\text{Mn,Cr})\text{O}_3$  at 1773 K in air showed that Cr doping to  $\text{LaMnO}_3$  is effective in increasing morphological stability. X-ray diffractometric results confirmed no reaction between Yttria Stabilized Zirconia (YSZ) and  $(\text{La,Sr})_{1-z}(\text{Mn,Cr})\text{O}_3$  after heated at 1773 K for 5 h in air. Electrical conductivities of the sintered samples were  $61.9 \text{ Scm}^{-1}$  and  $47.3 \text{ Scm}^{-1}$  at 1273 K in air for  $(\text{La}_{0.92}\text{Sr}_{0.08})\text{MnO}_3$  and  $(\text{La}_{0.92}\text{Sr}_{0.08})(\text{Mn}_{0.88}\text{Cr}_{0.12})\text{O}_3$ , respectively. Although overvoltage of  $(\text{La}_{0.92}\text{Sr}_{0.08})_{0.91}\text{MnO}_3$  air electrode increased from 0.09 V to 0.25 V at 1.0 A/cm<sup>2</sup> after a high temperature treatment (about 1673 K), this degradation was minimized with Cr doped electrodes; that is, overvoltage of  $(\text{La}_{0.92}\text{Sr}_{0.08})_{0.91}(\text{Mn}_{0.88}\text{Cr}_{0.12})\text{O}_3$  changed from 0.13 V to 0.18 V at 1.0 A/cm<sup>2</sup>. These results have suggested that  $(\text{La,Sr})_{1-z}(\text{Mn}_{1-y}\text{Cr}_y)\text{O}_3$  ( $0 < y \leq 0.2$ ) is one of appropriate air electrodes which can be used especially in a co-firing fabrication of SOFC.

### 1 INTRODUCTION

Solid Oxide Fuel Cells (SOFC) can be classified in terms of their structures into tubular, planar and honeycomb types. Among them, a planar SOFC will be the most suitable for large power plant utilization because the higher power density can be expected. Furthermore, well-established ceramic processing methods such as tape casting method can be applied to fabricate planar SOFC components cheaply and easily.

Recently, some attempts have been made to produce composite plates consisting of anode (Ni-YSZ) / electrolyte (YSZ) / cathode  $(\text{La}(\text{Sr})\text{MnO}_3)$  /

separator  $(\text{LaCr}(\text{Mg})\text{O}_3, \text{La}(\text{Ca})\text{CrO}_3)$  by co-firing of multilayer tape cast films<sup>1-2</sup>). In this process, sintering at a rather high temperature ( $>1673 \text{ K}$ ) is required to densify electrolyte and separator films; however, such a high temperature treatment causes degradation of performance of lanthanum manganite air electrode. This is due to the formation of poorly conductive compounds<sup>3-4</sup>),  $\text{La}_2\text{Zr}_2\text{O}_7$  or  $\text{SrZrO}_3$ , by reaction with Yttria Stabilized Zirconia (YSZ), and also due to the morphological change.

Recently, Yokokawa et al.<sup>5</sup>) reported that the reaction of  $\text{LaMnO}_3$  and YSZ originates from the thermodynamic nature of  $\text{LaMnO}_3$  having A-site deficiency<sup>6</sup>). Their thermodynamic analysis predicts that to avoid the reaction with YSZ, substantially A-site deficient manganites,  $(\text{La,Sr})_{1-z}\text{MnO}_3$  ( $z > 0$ ) may be preferential. However, preliminary experimental results showed that although substantially A-site deficient manganites actually did not react with YSZ, their sinterability was found to be higher

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than that of  $(\text{La,Sr})\text{MnO}_3$ . In order to repress the reaction with YSZ without losing the porosity of an electrode, some improvement can be expected by a so called 'material-design' approach based on substitution by other metals to B site as well as A site of the perovskite structure. As possible B site substituents, transition metal ions will be appropriate from viewpoint of the electrical properties. However, Yokokawa et al.<sup>7)</sup> reported that all lanthanum transition metal perovskites ( $\text{LaMO}_3$ ; M = transition metals) should react with YSZ at 1273 K except for Mn and Cr. Fortunately, lanthanum chromite ( $\text{LaCrO}_3$ ) is known to be ill-sinterable<sup>8)</sup>. After these considerations, we started to investigate air electrodes made of  $(\text{La,Sr})\text{CrO}_3$  and  $(\text{La,Sr})\text{MnO}_3$ . In this paper, sintering property, electrical conductivity and electrode catalytic activity of the  $(\text{La,Sr})\text{MnO}_3$ - $(\text{La,Sr})\text{CrO}_3$  perovskites are reported.

## 2 EXPERIMENTAL

### 2.1 Preparation

Sample powders were prepared by two methods. One is an usual powder mixing method; powders of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{MnCO}_3$  and  $\text{Cr}_2\text{O}_3$  were weighed in selected proportions and milled for 12 h with ethanol. After being dried, the mixed powders were pre-baked at 1273 K for 10 h in air, reground and baked at 1523 K for 5 h in air. The second preparation was made by nitrate method; aqueous solutions of  $\text{La}(\text{NO}_3)_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$  and  $\text{Cr}(\text{NO}_3)_3$  were mixed in selected proportions, and poured into ethanol solution of oxalic acid. The components of La, Sr and Mn were co-precipitated as oxalic salts; however, the Cr component was not co-precipitated completely in this stage, and therefore it was precipitated after drying up the solution by blowing air at room temperature. After organic compounds were burnt at 773 K for 5 h, samples were milled for 12 h with ethanol, reground and baked at 1273 K twice for 20 h in air. The sample powders made by the first powder mixing method were used in measurement of shrinkage and those made by the second method were used to measure electrical conductivities and electrode catalytic activities.

### 2.2 Sintering behavior

The samples were ground and pressed into pellets (40 mm in diameter) at 85 MPa. The sinterability of  $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Cr}_y\text{O}_3$  was evaluated from observed shrinkage after sintered at 1773 K for 2 h in air; the shrinkage was determined as  $(l_0-1)/l_0$ , where  $l_0$  and  $l$  are initial and final length, respectively.

### 2.3 Electrical conductivity

After sample powders were sintered at 1773 K for 2 h, they were cut into a rectangular shape (about 0.3 cm  $\times$  0.3 cm  $\times$  2.0 cm). Electrical conductivities were measured by four terminal method. After four platinum terminals attached using platinum paste, they were baked at 1273 K for 1 h. Measurements were made in air in the temperature region of 973-1373 K.

### 2.4 Electrode performance

The sample powders were coated on sintered pellets of YSZ (TOSOH, TZ-8Y; 8 mole percent  $\text{Y}_2\text{O}_3$ ) so that diameter of an effective electrode area is about 6 mm. They were baked at selected temperatures from 1423 to 1773 K in air. Electrical polarization measurements were made using current interruption technique<sup>9)</sup> at 1273 K in air after passing sufficient electric currents.

## 3 RESULTS AND DISCUSSION

### 3.1 Crystal structure of $\text{La}(\text{Mn,Cr})\text{O}_3$

$\text{LaMnO}_3$ <sup>10)</sup> and  $\text{LaCrO}_3$ <sup>11)</sup> have the perovskite structure ( $\text{ABO}_3$ ) in which A sites are occupied by  $\text{La}^{3+}$  ions, B sites being  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions or  $\text{Cr}^{3+}/\text{Cr}^{4+}$  ions;  $\text{LaMnO}_3$  has the hexagonal structure and  $\text{LaCrO}_3$  is orthorhombic at 1273 K in air.

Analysis on X-ray diffractometric patterns of the pseudobinary system clarified that all peaks observed can be ascribed to lines associated either with hexagonal perovskite structure ( $0 \leq y \leq 0.3$ ) or with orthorhombic perovskite structure ( $0.4 \leq y \leq 1.0$ ); no peak was observed for other phases. It can be thus concluded that  $\text{La}(\text{Mn}_{1-y}\text{Cr}_y)\text{O}_3$  forms solid solutions over the whole composition range of  $y$ . The phase transformation from the hexagonal to the orthorhombic symmetry was observed in the vicinity of  $0.3 \leq y \leq 0.4$ . This agrees with recent experimental results

by Anderson et al.<sup>12</sup>). Figure 1 shows the lattice parameters of  $\text{LaMn}_{1-y}\text{Cr}_y\text{O}_3$  having the hexagonal symmetry as a function of Cr content ( $y$ ). With increasing Cr content, the lattice parameters  $a$  and  $c$  gradually decreased because the  $\text{Cr}^{3+}$  ion radius in the octahedral site (0.0615 nm) is smaller than that of  $\text{Mn}^{3+}$  ions (0.0645 nm). In Fig. 1, the closed circles represent the

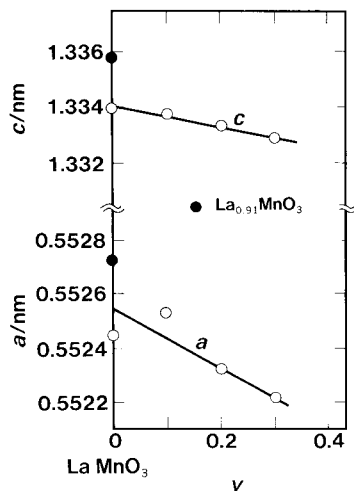


Fig. 1 The lattice parameter as a function of Cr content ( $y$ ).

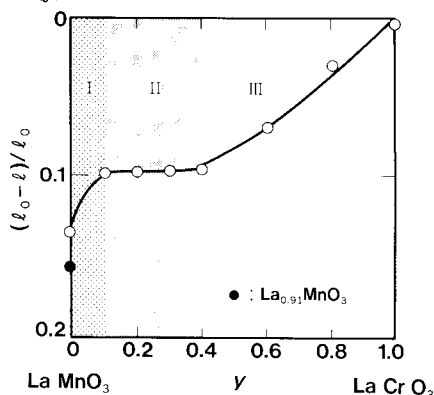


Fig. 2 Shrinkage of  $\text{LaMn}_{1-y}\text{Cr}_y\text{O}_3$ .

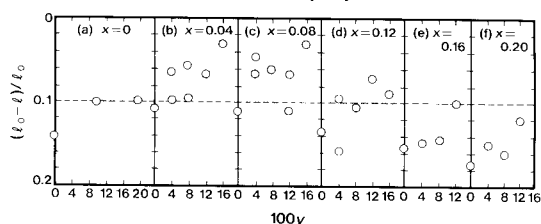


Fig. 3 Shrinkage of  $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Cr}_y\text{O}_3$  as a function of Cr content ( $y$ ) with a parameter of Sr content ( $x$ ).

A-site deficient perovskite,  $\text{La}_{0.91}\text{MnO}_3$ . Its lattice parameters are larger than those of non A-site deficient  $\text{LaMnO}_3$ .

### 3.2 Sintering behavior of $(\text{La,Sr})(\text{Mn,Cr})\text{O}_3$

Figure 2 shows observed shrinkage of  $\text{LaMn}_{1-y}\text{Cr}_y\text{O}_3$  pellets after heated at 1773 K for 2 h in air. The sinterability decreased with increasing Cr substitution at B sites. It should be noted that remarkable decrease in shrinkage was observed with only a small amount of Cr doping (region I:  $0 \leq y \leq 0.1$ ). In region II ( $0.1 < y \leq 0.4$ ), shrinkage was independent of Cr content. In region III ( $0.4 < y \leq 1.0$ ), shrinkage decreased linearly with Cr content and finally approached almost zero at  $y=1$ , namely  $\text{LaCrO}_3$ . Since cathodic polarization of lanthanum chromite is quite large<sup>13</sup>), heavy Cr doping will not be appropriate for an air electrode. Thus, further investigations have been made mainly in the composition region I.

Since alkaline earth ions are usually doped in  $\text{LaMnO}_3$ -based air electrode to enhance the electrical conductivity, sintering shrinkage of the  $(\text{La}_{1-x}\text{Sr}_x)(\text{Mn}_{1-y}\text{Cr}_y)\text{O}_3$  system ( $0 \leq x \leq 0.2$ ,  $0 \leq y \leq 0.2$ ) was examined in details; results are summarized in Fig. 3 as a function of Cr content ( $y$ ) with a parameter of Sr content ( $x$ ). For each Sr content, the common tendency can be seen in Fig. 3; that is, the high Cr doping lowers shrinkage. This feature is not influenced by Sr substitution. Note that when Sr is doped to lanthanum manganites,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , the sinterability initially decreased with increasing Sr substitution in the region of  $0 < x \leq 0.08$ , and in the region of  $x > 0.08$ , in turn increased. Thus, the smallest shrinkage was obtained at the Sr content around  $0.04 \leq x \leq 0.08$ . This behavior seems to relate to changes in vacancies of cations and oxygen ions, although details remain uncertain.

### 3.3 Reaction with YSZ

Yokokawa et al.<sup>5)</sup> suggested from thermodynamic analysis that the stoichiometric  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  should react with YSZ even at 1473 K, whereas substantially A-site deficient  $(\text{La,Sr})_{1-z}\text{MnO}_3$  do not give rise to reaction. We tried to confirm it experimentally. After lanthanum manganites were mixed with YSZ, they were baked at

high temperatures (above 1273 K) in air. We confirmed by X-ray diffractometry that the stoichiometric lanthanum manganite reacted with YSZ at 1473 K for 5 h and the A-site deficient lanthanum manganite did not react at 1773 K for 5 h.

We also investigated the reaction of ill-sinterable Cr doped lanthanum manganite and YSZ. Reactivity of  $(La_{1-x}Sr_x)(Mn_{1-y}Cr_y)O_3$  and YSZ changed noticeably on Cr doping. The chromium doped manganites without A-site deficiency ( $x=0.2$ ,  $0.08 \leq y \leq 0.2$ ) did not react with YSZ at 1473 K for 5 h in air. A-site deficient perovskites  $(La_{1-x}Sr_x)_{0.91}(Mn_{1-y}Cr_y)O_3$  did not react even at 1773 K for 5 h, neither.

### 3.4 Electrical conductivity

The temperature dependence of electrical conductivities of  $AMn_{1-y}Cr_yO_3$  ( $A=La_{0.92}Sr_{0.08}$ ) is shown in Fig. 4.

For the case of  $y=0$ , the electrical conductivity of  $AMnO_3$  was metallic, whereas the A-site deficient perovskite,  $A_{0.91}MnO_3$ , exhibited semiconductive. Note however that the electrical conductivities of  $A_{0.91}MnO_3$  were affected by its phase transformation around 1423 K. Above that temperature,  $A_{0.91}MnO_3$  has the orthorhombic symmetry, and undergoes the transformation to the hexagonal phase about 1423 K. This transformation was confirmed by differential thermal analysis and X-ray analysis. Since this transformation proceeds slowly, the electrical conductivities of the orthorhombic phase were measured

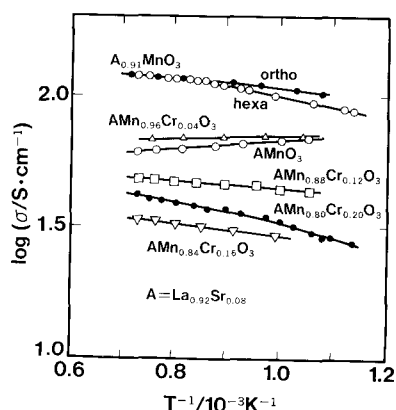


Fig. 4 Electrical conductivity in the  $AMnO_3$ - $ACrO_3$  ( $A=La_{0.92}Sr_{0.08}$ ) system.

even below 1423 K as shown in Fig. 4 (closed circles); electrical conductivities represented by open circles were determined for samples after being well annealed.

In the region of  $0 < y \leq 0.2$ , heavy Cr doping decreased the electrical conductivity. Table 1 shows electrical properties and relative densities of the present samples.  $(La,Sr)CrO_3$  is known to be semiconductive, while  $(La,Sr)MnO_3$  is metallic. This leads to an expectation that Cr doping to  $AMnO_3$  may cause some lowering of the electrical conductivities. Observed lowering of electrical conductivity was, however, not drastic. On the other hand, the relative densities of the present samples given in Table 1 show a good correlation with the observed electrical conductivities. Since the relative densities of the present samples are rather small, further investigations should be needed to clarify effects of Cr doping on electrical conductivities.

It should be noted that the electrical conductivity changed from metallic to semiconductive on heavy Cr doping ( $y \leq 0.08$ ). This semiconductive  $AMn_{0.80}Cr_{0.20}O_3$  exhibited a slight change in temperature dependence to the semiconductive  $A_{0.91}MnO_3$ . This is due to the transformation from the high-temperature hexagonal to the low-temperature phase. This transformation was confirmed by DTA on well-annealed samples just below the transformation temperature. Since it takes a long time to undergo this transformation at the low temperature (about 923 K), electrical conductivities shown in Fig. 4 can be interpreted as those of the mixed phases.

Table 1 Measured electrical conductivity at 1273 K,  $\sigma$ , and relative density,  $\rho/\rho_0$ , for  $AMn_{1-y}Cr_yO_3$  ( $A=La_{0.92}Sr_{0.08}$ ).

Compound	$\sigma$ (S/cm)	$\rho/\rho_0$	Conductive mechanism
$A_{0.91}MnO_3$	116.7	91	semiconductive
$AMnO_3$	61.9	70	metallic
$AMn_{0.96}Cr_{0.04}O_3$	68.4	75	metallic
$AMn_{0.88}Cr_{0.12}O_3$	47.3	70	semiconductive
$AMn_{0.84}Cr_{0.16}O_3$	33.5	63	semiconductive
$AMn_{0.80}Cr_{0.20}O_3$	40.6	68	semiconductive

### 3.5 Electrode catalytic activity

The DC polarization measurements were made for the stoichiometric perovskites,  $(La_{1-x}Sr_x)(Mn_{1-y}Cr_y)O_3$ ; these samples showed poor electrode catalytic activities. An important point is that in some cases, electrodes were detached from YSZ pellets because of weak bonding between electrode and YSZ as a result of ill-sinterability of electrode materials. For comparison, we also measured the electrode activity of A-site deficient lanthanum manganite,  $(La_{1-x}Sr_x)_{0.91}(Mn_{1-y}Cr_y)O_3$ , which was confirmed to be more sinterable than stoichiometric  $(La_{1-x}Sr_x)(Mn_{1-y}Cr_y)O_3$ .

Figure 5 shows polarization curves of  $A_{0.91}(Mn_{0.88}Cr_{0.12})O_3$  and  $A_{0.91}MnO_3$  ( $A = La_{0.92}Sr_{0.08}$ ) at 1273 K in air. When  $A_{0.91}MnO_3$  was baked at a high temperature (1673 K) for 4 h, the electrode performance considerably degraded; compare 0.25 V at 1.0 A/cm<sup>2</sup> with 0.09 V obtained for the electrode baked at 1423 K for 4 h. This is apparently due to the change in morphology of electrode during the high temperature heat treatment. Observed effects of Cr doping on electrode catalytic activity are quite interesting from the viewpoint of the morphological stability. When Cr-doped  $A_{0.91}(Mn_{0.88}Cr_{0.12})O_3$  was compared with the non Cr-doped sample, it showed lower activities (0.13 V vs. 0.09 V at 1.0 A/cm<sup>2</sup>) for 1423 K, and much higher activities (0.25 V vs. 0.18 V at 1.0 A/cm<sup>2</sup>) for baking at 1673 K. This indicates that the Cr-doping to lanthanum manganite can be effective in increasing morphological stability during high temperature heat treatment. This

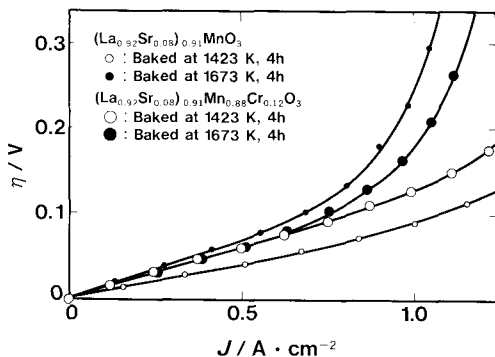


Fig. 5 Polarization curves of  $A_{0.91}Mn_{0.88}Cr_{0.12}O_3$  and  $A_{0.91}MnO_3$  ( $A = La_{0.92}Sr_{0.08}$ ) at 1273 K.

effect of keeping the electrode porosity would be appropriate for fabricating SOFC by co-firing method in which the highest temperature will be 1673-1723 K.

## 4 CONCLUSION

We have found that Cr-doped manganites,  $(La,Sr)_{1-x}(Mn_{1-y}Cr_y)O_3$  ( $0 < y \leq 0.2$ ), repressed the degradation of electrode activity and the reaction with YSZ on high-temperature baking. The present new materials provide some feasibility of producing SOFC by co-firing process in which air electrodes are inevitably heated with YSZ at high temperatures.

## REFERENCES

- 1) N. Q. Minh, Proceedings of the SOFC-NAGOYA, November 1989, Nagoya, pp.37-41.
- 2) M. Dokiya, N. Sakai, T. Kawada, H. Yokokawa, T. Iwata and M. Mori, 24th IECEC, August 1989, Washington, D.C., pp.1547-1551.
- 3) O. Yamamoto, Y. Takeda, R. Kanno, and T. Kojima, Proceedings of the First International Symposium on SOFC, ed. S. C. Singhal, The Electrochemical Society, October 1989, Hollywood, Florida, pp.242-253.
- 4) R. Okuyama, H. Hayamizu, M. Fukuda, T. Ishihara, Y. Asano, H. Inukai, N. Nishikawa, H. Nishikawa, H. Yoshida, and M. Narita, Proc. 56th spring meeting of Chem. Soc. Japan, pp.195(1989).
- 5) H. Yokokawa, N. Sakai, T. Kawada and M. Dokiya, *Denki Kagaku* 57(8), 829(1989).
- 6) J. Shimoyama, J. Mizusaki and K. Fueki, Proc. 53rd fall meeting of Chem. Soc. Japan, pp.263(1988).
- 7) H. Yokokawa, N. Sakai, T. Kawada and M. Dokiya, *Denki Kagaku* 57, 821(1989).
- 8) L. Group and H. U. Anderson, *J. Am. Ceram. Soc.*, 59, 449(1976).
- 9) Da Yu Wang and A. S. Nowick, *J. Electrochem. Soc.*, 126(7), 1155(1979).
- 10) A. Hammouche, E. Siebert and A. Hammou, *Mat. Res. Bull.*, 24, pp.367-380(1989).
- 11) C. P. Khattak and D. E. Cox, *Mat. Res. Bull.*, 12, 463(1977).
- 12) R. Koc, H. U. Anderson and S. A. Howard, Proceedings of the First International Symposium on SOFC, ed. by S.C. Singhal, The Electrochemical Society, October 1989, Hollywood, Florida, pp.220-241.
- 13) Y. Takeda, O. Yamamoto, M. Noda and R. Kanno, *J. Electrochem. Soc.*, 134, 2565(1987).